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Curtin

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[54] ELECTROPHOTOGRAPHIC ELEMENT WHICH INCLUDES A PHOTOCONDUCTIVE POLYVINYL CARBAZOLE LAYER CONTAINING AN ALICYCLIC ANHYDRIDE

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[51] **Int. Cl.^{2}** **G03G 5/04**
[58] **Field of Search** 96/1.5; 252/501

[56] **References Cited**

UNITED STATES PATENTS

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[57] ABSTRACT

For use in an electrophotographic copy process, a photoconductive element formed of an organic photoconductive composition on a suitable substrate, in which the speed and charge retention of the organic photoconductor, preferably a polymerized vinyl carbazole and 2,4,7-trinitro-9-fluorenone, is improved by the presence of an alicyclic anhydride in an amount within the range of 0.01% to 1.0% by weight of the coated solids.

12 Claims, No Drawings

ELECTROPHOTOGRAPHIC ELEMENT WHICH INCLUDES A PHOTOCONDUCTIVE POLYVINYL CARBAZOLE LAYER CONTAINING AN ALICYCLIC ANHYDRIDE

This invention relates to photoconductors and more particularly to an organic photoconductor composition for use in the preparation of photoconductive elements in the production of copy by the electrophotographic process.

In the electrophotographic copy process, use is made of a photoconductive surface onto which a uniform electrostatic charge is applied. The charge is retained on the surface except for those areas that are rendered conductive during exposure to a light pattern, leaving a latent electrostatic image on the non-exposed portions of the photoconductive surface. The latent electrostatic image is subsequently developed in a conventional manner, as by means of a dry developing powder which is cascaded over the surface, or by a liquid developer or toner suspended in an insulating liquid with which the plate surface is wet. Instead, the latent electrostatic image can be transferred to a copy sheet for development of the image thereon, as by a liquid or powder developer.

To the present, especially in relatively high speed copy machines, amorphous selenium, with or without an added dopant, has been used to provide the photoconductive surface on a suitable support. While selenium provides a photoconductive surface having the desired speed and sensitivity for use in high speed copy machines, selenium represents a relatively expensive material which is difficult to apply, and its use as a photoconductive composition is somewhat restricted to a support formed of a rigid material such as a metal drum or plate.

There is considerable interest in a low cost organic photoconductive composition which might be applied by conventional coating techniques, for use on various supports, such as on an endless belt, flexible paper, metal or plastic strip, and the like, as well as on a rigid metal drum or plate.

While organic photoconductors offer advantages of the type described, they are also faced with a number of disadvantages in that organic photoconductors, which have been suggested to the present, are characterized by low charge acceptance and lesser sensitivity by comparison with selenium.

In U.S. Pat. No. 3,484,237, description is made of an organic photoconductor composition formed of a polymerized vinyl carbazole compound to which 2,4,7-trinitro-9-fluorenone has been added as an electron acceptor to lower the dark conductivity of the photoconductive layer and to increase the sensitivity in the visible range.

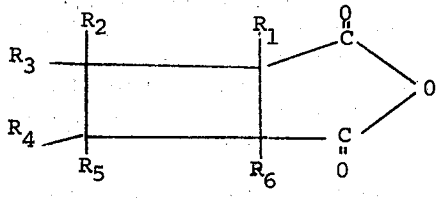
Organic photoconductors of the type described are capable of copy speeds in the range of 10 to 25 copies per minute.

It is, of course, desirable to increase the copy speed of organic photoconductors to a rate considerably in excess of 25 copies per minute. This can be accomplished by increase in the charge acceptance of the photoconductor as well as in the photoconductivity or light sensitivity of the photoconductor, as measured by light decay sensitivity of the charge on the photoconductive surface, as the result of light exposure.

It has been found, in accordance with the practice of this invention, that the charge acceptance and sensitivity of organic photoconductors can be markedly increased when the organic photoconductor is formulated to contain an alicyclic anhydride. The improvement in charge acceptance and sensitivity, as measured by charge decay, is particularly significant when the alicyclic anhydride is present in an organic photoconductor composition formulated of a polymerized vinyl carbazole (PVK) in 2,4,7-trinitro-9-fluorenone (TNF), to form photoconductive coatings of the charge-transfer complex types.

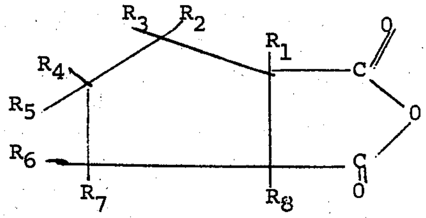
As the alicyclic anhydride, it is preferred to make use of one or more of the following:

a. Cyclobutanedicarboxylic anhydrides



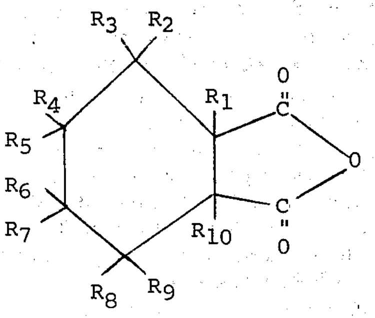
wherein R_{1-6} are hydrogen, lower alkyl groups, such as methyl, ethyl, propyl, etc., halogen such as chlorine, bromine and iodine, hydroxy or nitro groups. R_{1-6} can be the same or different. R_2 and R_4 can also be an anhydride functional group. Representative of such anhydrides are such compounds as 1-2,cyclobutanedicarboxylic anhydride, including the cis and trans isomers thereof, 1,2,3,4-cyclobutanetetracarboxylic-1,2,3,4-dianhydride, 1,2,3,4-tetramethyl-1,2-cyclobutanedicarboxylic anhydride, 3-chloro-3-methyl-1,2-cyclobutanedicarboxylic anhydride, and 1,4-dimethyl-1,2,3,4-cyclobutanetetracarboxylic dianhydride.

b. Cyclopentanedicarboxylic anhydrides



where R_{1-8} are hydrogen, lower alkyl groups such as methyl, ethyl, propyl, butyl, etc., halogen such as chlorine, bromine, iodine, hydroxy or nitro, in which R_{1-8} can be the same or different. R_2 and R_4 can also be an anhydride functional group. Representative of such cyclopentanedicarboxylic anhydrides are 1,2-cyclopentanedicarboxylic anhydride, 3,3-dimethyl-1,2-cyclopentanedicarboxylic anhydride, 4,5-dihydroxy-1,2-cyclopentanedicarboxylic anhydride, 1-methyl-1,2-cyclopentanedicarboxylic anhydride, cis, cis, cis, cis-1,2,3,4-cyclopentanetetracarboxylic dianhydride.

c. Cyclohexanedicarboxylic anhydrides



where R_{1-10} can be hydrogen, lower alkyl groups such as methyl, ethyl, propyl, etc., halogen such as chlorine, bromine, iodine, etc., hydroxy, nitrile or nitro groups. R_{1-10} can be the same or different and R_2 and R_4 as well as R_6 and R_8 can be an anhydride functional group. Representative of such cyclohexanedicarboxylic anhydrides are 1,2-cyclohexanedicarboxylic anhydride, and their cis and trans isomers, cis-1,2-dimethyl-1,2-cyclohexanedicarboxylic anhydride, trans-1,2-dimethyl-1,2-cyclohexanedicarboxylic anhydride, 1,2,4,5-cyclohexanetetracarboxylic-1,2,4,5-dianhydride, and 1,2,3,4,5,6-cyclohexanehexacarboxylic 1,2:3,4:5,6-trianhydride.

Suitable alicyclic anhydrides range from anhydrides having at least 3 carbon atoms in the alicyclic group as represented by 1,2-cyclopropanedicarboxylic anhydride, to and including anhydrides, dianhydrides and polyanhydrides having up to 18–20 carbon atoms in the cyclic group, although it is preferred to make use of anhydrides having substituents as described in (a), (b) and (c) above, in which the number of carbon atoms in the alicyclic group are within the range of 4–10, as represented by the foregoing as well as a 1,2-cycloheptanedicarboxylic anhydride and 1,2-cyclodecanedicarboxylic anhydride.

Noticeable improvement is observed when the alicyclic anhydride is employed in the photoconductive composition in an amount of at least 0.01% by weight of the coating solids to as much as 1.0% by weight of the coating solids, but it is preferred to make use of an amount within the range of 0.02% to 0.5% by weight of the total sum of PVK and TNF.

The following represent the polymerized vinyl carbazole compounds which may be used in the formulation of the organic photoconductive coatings of this invention, namely: poly-N-vinyl carbazole and polyvinyl-N-lower alkyl carbazoles of the type described in the U.S. Pat. No. 3,484,237. The following can be given by way of examples of suitable poly-N-lower alkyl carbazoles, namely, poly-2-vinyl-N-methylcarbazole, poly-3-vinyl-N-ethylcarbazole, poly-2-vinyl-N-ethylcarbazole, poly-3-vinyl-N-methylcarbazole, poly-3-vinyl-N-isopropylcarbazole, poly-2-vinly-N-butylcarbazole, poly-3-vinyl-N-butylcarbazole, poly-2-vinyl-N-pentylcarbazole, poly-3-vinyl-N-pentylcarbazole, poly-2-vinyl-N-hexylcarbazole, poly-3-vinyl-N-hexylcarbazole, poly-2-vinyl-N-heptylcarbazole, and poly-3-vinyl-N-heptylcarbazole. Mixtures and copolymers of the polymerized vinylcarbazole compounds also may be used.

When the organic photoconductor is of the charge-transfer type formulated of polymerized vinyl carbazoles and 2,4,7-trinitro-9-fluorenone, the ingredients are formulated into the coating composition in the ratio of about 0.49 to 1.3 moles of TNF per monomer unit of PVK, which ratio will continue in the organic photoconductor that is formed upon coating a suitable substrate and then dried to cure the coating onto the substrate.

As the substrate, use can be made of a rigid plate or drum formed of glass or of a metal such as aluminum having a silicated surface and the like, or the substrate upon which the photoconductive coating is applied may be a flexible element, such as a plate, drum, or endless belt formed of paper, plastic, metal-paper laminate, or a sheet of silicated aluminum or the like.

The materials are formulated into a composition for coating onto a suitable substrate by first dissolving the polyvinylcarbazole component in a suitable solvent, such as tetrahydrofuran, and then admixing the solution of the polyvinylcarbazole with the 2,4,7-trinitro-9-fluorenone and alicyclic anhydride, preferably in solution in the same solvent, and any additional solvent required to achieve the desired consistency for the coating composition. The materials may be worked into solution on a roller mill and the like and coated onto the substrate by conventional coating means, followed by air drying and then curing at elevated temperature such as for one hour at 50°–60°C. Instead of tetrahydrofuran, other solvents such as 1,2-dichloroethane and chlorobenzene may be used.

The photoconductive compositions of the present invention are useful in the conventional xerographic process in which an electrostatic image is formed on the surface of the photoconductive element and the electrostatic image is subsequently developed. In practice, the photoconductive element is electrostatically charged and exposed to a pattern of light and dark to form an electrostatic image. Thereafter, the electrostatic image can either be developed with a conventional electroscopic powder developer on the photoconductive element and the developed image transferred to plain paper, or the electrostatic image can be transferred to a dielectric paper for development with an electroscopic developer (powder or liquid).

The following examples are given by way of illustration, but not by way of limitation, of the practice of the invention:

EXAMPLE 1

In this example, comparison is made between an organic photoconductor embodying the features of this invention, with a photoconductor of identical composition except for the omission of the alicyclic acid anhydride component.

For this purpose, a mixture was prepared of the following ingredients:

24.8 grams 2,4,7-trinitro-9-fluorenone

200 ml tetrahydrofuran (previously dried over sodium)

160 ml poly-N-vinylcarbazole in 10% solution in tetrahydrofuran

Solution was effected by roller milling until dissolved. The batch was divided into two equal segments, hereinafter identified as 1(*a*) and 1(*b*).

Each segment was diluted with equal volumes of tetrahydrofuran to reduce the materials to coating viscosity. 2 ml of a 1% solution of cis-1,2-cyclobutanedicarboxylic acid anhydride in tetrahydrofuran was added to segment 1(*b*).

The coating compositions were applied onto separate silicated aluminum belts having a thickness of 3.5 mils. Coating was effected by mounting the belts on a drum operated for rotational movement about a horizontal axis. Application was made by means of an air brush mounted a fixed distance from the surface of the belt and displaced crosswise over the surface of the belt in increments of 2 mm per revolution, and operated under a pressure of 18 psi with nitrogen. An amount was applied to form a dried coating having a thickness of about 10–12 microns.

The coated plates were allowed to air dry and then they were cured for 1 hour at 50°C.

The plates were each tested for charge acceptance and charge retention by exposing the plates to negative electrostatic corona charge of 6 kv by passing the plates beneath charging wires. Charge acceptance and charge retention were measured by a Monroe electrometer which measures the charge on the surfaces of the plates in volts.

The plates were also each tested for sensitivity by the use of the Monroe electrometer to measure the amount of charge dissipated by light exposure. For this purpose, exposure was made with a tungsten photoenlarger lamp of 150 watts operating through an enlarger. Energy of exposure identifies the amount of light that fell on the plate in $\mu J/cm^2$, as measured by a Hewlett-Packard radiant flux meter.

The following values were obtained with the plates of Examples 1(*a*) and 1(*b*):

Example	Charge acceptance in volts	Sensitivity in $Vcm^2/\mu J$
1 (a)	130	3.0
1 (b)	650	18.7

The sensitivity values given above were for the average of exposures at 7, 14 and 28 $\mu J/cm^2$.

It will be apparent from the above that the addition of the alicyclic acid anhydride gave an improvement of 500% in charge acceptance and 623% in sensitivity.

Plates prepared of a composition corresponding to Example 1(*b*) gave a dark decay rate of 3.0 volts per second.

The amount of conductive coating applied to the substrate is not significant. The desired results can be obtained in coating weights sufficient to provide coating thickness of 5 microns; however, it is undesirable from the standpoint of economics and flexibility of the coating to exceed a coating thickness of about 30 microns. In the preferred practice of this invention, use is made of the organic photoconductor in dry coatings having a thickness within the range of 8 to 15 microns.

With plates embodying the features of this invention, copies have been produced by the electrostatic technique at copy speeds considerably greater than 25 copies per minute and up to as many as 60 copies per minute.

The terms "carboxylic acid anhydride" and "carboxylic anhydride" are used by the skilled in the art and in this application to identify the same compound.

It will be understood that changes may be made in the details of formulation, construction and operation without departing from the spirit of the invention, especially as defined in the following claims.

I claim:

1. In an electrophotographic element for use in an electrophotographic copy process formed of a substrate having an organic photoconductive coating formed of 2,4,7-trinitro-9-fluorenone and a polymerized vinyl carbazole present in the ratio of 0.49 to 1.23 moles of the trinitro fluorenone per monomeric unit of polymerized vinyl carbazole on one surface, the improvement wherein an alicyclic anhydride is incorporated into the organic photoconductive composition whereby the charge retention and sensitivity of the photoconductive coating is markedly improved to increase copy speed.

2. An electrophotographic element as claimed in claim **1** in which the alicyclic anhydride is present in the coating in an amount within the range of 0.01% to 1.0% by weight of the coating solids.

3. An electrophotographic element as claimed in claim **1** in which the alicyclic anhydride is present in the coating in an amount within the range of 0.02% to 0.5% by weight of the coating solids.

4. An electrophotographic element as claimed in claim **1** in which the photoconductive coating is of a thickness within the range of 5–30 microns.

5. An electrophotographic element as claimed in claim **1** in which the photoconductive coating is of a thickness within the range of 8–15 microns.

6. An electrophotographic element as claimed in claim **1** in which the polymerized vinyl carbazole is poly-N-vinyl carbazole.

7. An electrophotographic element as claimed in claim **1** in which the cyclic group of the alicyclic anhydride is selected from the group consisting of cyclobutane, cyclopentane and cyclohexane, and substituents thereof.

8. An organic photoconductive composition for use in the preparation of a photoconductive coating from which copies can be produced by an electrophotographic process, in which the composition consists essentially of an organic photoconductor and 0.1% to 1.0% by weight (based on coating solids) of an alicyclic anhydride having from 3 to 20 carbon atoms in the alicyclic group.

9. A composition as claimed in claim **8** in which the organic photoconductor comprises 2,4,7-trinitro-9-fluorenone and a polymerized vinyl carbazole present in the ratio of about 0.49 to 1.23 moles of the trinitro fluorenone per monomeric unit of the polymerized vinyl carbazole and in which the materials are present in solution in an organic solvent.

10. A composition as claimed in claim **9** in which the alicyclic anhydride is present in an amount within the range of 0.02% to 0.5% by weight of the coated solids.

11. A composition as claimed in claim **9** in which the organic solvent in which the photoconductive materials are dissolved is tetrahydrofuran.

12. A composition as claimed in claim **8** in which the alicyclic group of the alicyclic anhydride is selected from the group consisting of cyclobutane, cyclopentane and cyclohexane, and derivatives thereof.

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